Journal of Organometallic Chemistry, 190 (1980) C101—C104
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SOME CHEMISTRY OF MIXED LIGAND COMPLEXES OF PLATINUM

HOWARD C. CLARK*, ANIL B. GOEL and CHUN S. WONG
Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1 (Canada)

(Received December 18th, 1979)

Summary

Simple synthetic routes to the mixed ligand complexes $PtLL'X_2$ and $PtLL'XY$ ($L' = PEt_3$; L = phosphine, arsine, etc.; X = Cl and Y = Cl, H or Me) are described; unexpectedly, these display an extensive chemistry without disproportionation, although in some cases ligand scrambling does occur.

The preparation of metal complexes of low symmetry containing readily available ligands can greatly benefit studies of (a) asymmetric synthesis catalyzed by metal complexes, and (b) electronic and steric effects of ligands on the catalytic activity of metal complexes. Particularly for those species containing monodentate ligands, the tendency towards disproportionation to more symmetrical complexes, has obviously deterred investigation, e.g. for platinum(II)

$$2\,PtLL'X_2 \rightarrow PtL_2X_2 + PtL_2'X_2$$

However, in a low symmetry species such as *trans*-$PtLL'XY$, the ability to vary systematically, just one ligand L′, would open a unique method to study steric and electronic ligand effects, especially for those complexes which catalyze organic transformations.

There have been only a few scattered reports [1,2] of such platinum(II) complexes, most of which have been dichlorides*. Hitherto, the extent to which their full chemistry can be developed without the occurrence of extensive disproportionation** has not been determined. We now describe a simple route to such low symmetry platinum(II) complexes containing readily available monodentate ligands, and demonstrate the extent of their potentially interesting chemistry.

Dropwise addition of a solution of L ($L = PPh_3$, $PMePh_2$, P-i-Pr_3, PCy_3, $AsPh_3$ or $SbPh_3$) to a dichloromethane solution of $[PtL'Cl_2]_2$ ($L' = PEt_3$) resulted in the formation of the lemon-yellow crystalline *trans*-$PtLL'Cl_2$, except for L =

---

*Preparation of PtRClLL′ (R = phenyl) has been described recently [3].

**For example, the preparation of $Pt(P\text{-}n\text{-}Bu_3)(PEt_3)Cl_2$ [2] leads to impure products.

$SbPh_3$ in which case the *cis* isomer is obtained. *trans*-Pt(PEt_3)LCl_2 (L = PPh_3, $PMePh_2$, $AsPh_3$), when suspended in a small amount of dichloromethane in the presence of a catalytic amount of L, isomerized to the *cis* isomer. Isomerization is usually complete in 2—3 h to give the *cis* isomer in excellent yield (95—100%). The ^{31}P NMR spectrum showed that no observable disproportionation had occurred.

Hydrazine reduction of *cis*-PtLL′Cl_2 (L′ = PEt_3, L = PPh_3, $PMePh_2$ or $AsPh_3$) in refluxing ethanol led to extensive disproportionation. However, reduction with $NaBH_4$ [4] at 0°C followed by acidification with HCl afforded the mixed-ligand hydrides (equations 1—3).

$$\textit{cis}\text{-Pt(PPh}_2\text{Me)(PEt}_3\text{)Cl}_2 \xrightarrow{\substack{1.\ \text{NaBH}_4\\ 2.\ \text{HCl}}}$$

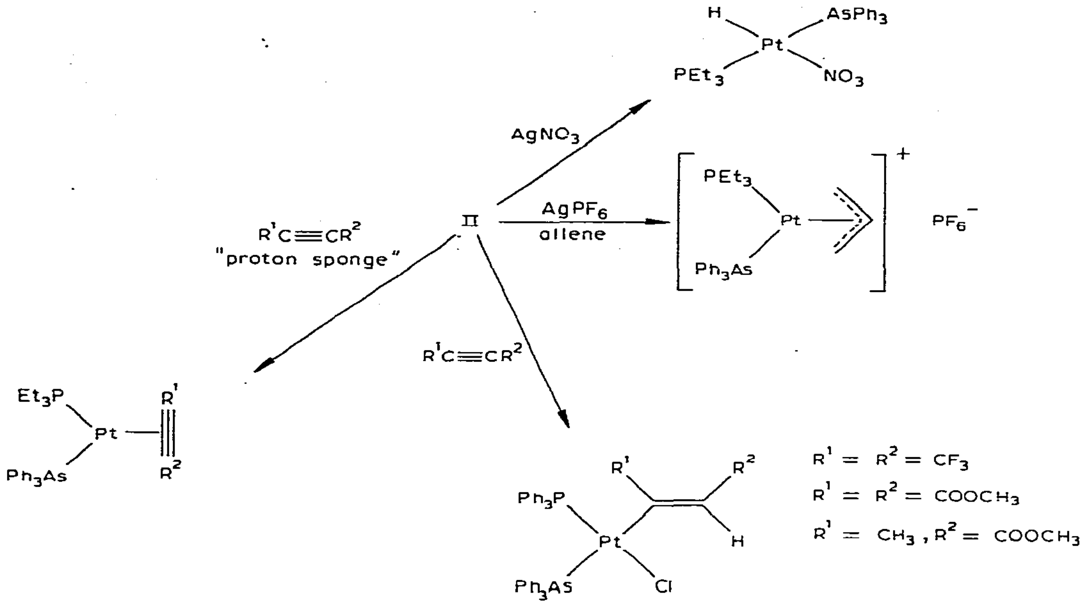
$$\underset{2}{\text{HPt(PMePh}_2\text{)(PEt}_3\text{)Cl}} + \underset{:\ 1\ :}{\text{HPt(PMePh}_2\text{)}_2\text{Cl}} + \underset{1}{\text{HPt(PEt}_3\text{)}_2\text{Cl}} \qquad (1)$$

$$\textit{cis}\text{-Pt(PPh}_3\text{)(PEt}_3\text{)Cl}_2 \xrightarrow{\substack{1.\ \text{NaBH}_4\\ 2.\ \text{HCl}}}$$

$$\underset{4}{\text{HPt(PPh}_3\text{)(PEt}_3\text{)Cl}} + \underset{:\ 1\ :}{\text{HPt(PPh}_3\text{)}_2\text{Cl}} + \underset{1}{\text{HPt(PEt}_3\text{)}_2\text{Cl}} \qquad (2)$$

$$\textit{cis}\text{-Pt(PEt}_3\text{)(AsPh}_3\text{)Cl}_2 \xrightarrow{\substack{1.\ \text{NaBH}_4\\ 2.\ \text{HCl}}} \text{HPt(PEt}_3\text{)(AsPh}_3\text{)Cl} \qquad (3)$$

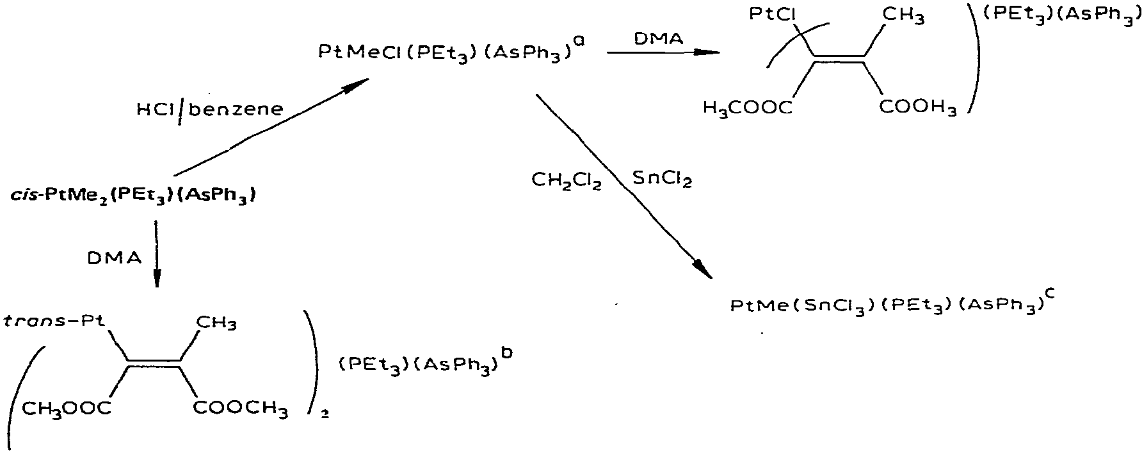
Some ligand scrambling occurs, the extent of which depends on the nature of the ligands L and L′. The less alike the two ligands are, the smaller is the extent of disproportionation. Thus, for L′ = PEt_3 and L = $PMePh_2$, there is about 50% disproportionation, about 34% for L′ = PEt_3 and L = PPh_3, and 0% for L′ = PEt_3 and L = $AsPh_3$ (77% yield of hydridochloride). Both HPt(PPh_3)(PEt_3)Cl (I) (^1H NMR δ(PtH) −17.1 triplet, J(PH) 14.0, J(PtH) 1271.4 Hz; ^{31}P NMR δ 24.4, J(PtP) 2852 Hz, δ 25.3, J(PtP) 2825 Hz) and HPt(PEt_3)($AsPh_3$)Cl (II) (^1H NMR δ(PtH)) −18.4 ppm doublet, J(PtH) 1016 Hz, J(PH) 12.5 Hz; ^{31}P NMR δ 19.00, J(PtP) 3530.3 Hz) are fairly stable towards disproportionation in solution; I disproportionates only slightly (< 5%) in $CDCl_3$ over a period of 3 days, while II shows no signs of disproportionation over the same time. Both I and II undergo the usual type of hydride reactions. Thus, metathetical displacement occurs in the reaction of II with $AgNO_3$ to give HPt(PEt_3)($AsPh_3$)(NO_3) (Pt—H δ −24.6, J(PtH) 1260, J(PH) 14 Hz; ^{31}P NMR, δ(P) 21.61, J(PtP) 3415.)) Also, in the presence of $AgPF_6$, allene reacts with II to give a static π-allyl complex at room temperature, and activated acetylenes insert into the Pt—H bond of II forming σ-alkenyl products. Although, in the latter type of reaction, a large number of isomeric products is possible, only one isomer is formed (Scheme 1) e.g. for R^1 = CH_3, R^2 = $COOCH_3$, ^1H NMR gives R^1 δ 2.17, ^3J(PtH) 48 Hz, ^4J(HH) 1.4 Hz, and R^2 δ 3.52; ^{31}P NMR, δ 10.76, J(PtP) 3727 Hz.



SCHEME 1

Again reaction of II with an activated acetylene such as dimethylacetylenedicarboxylate (DMA) in the presence of proton sponge, gives the acetylene-platinum(0) complex with mixed ligands.

Similarly, the *cis* mixed-ligand dichlorides react with excess methyllithium in ether to afford the complexes $PtMe_2LL'$ ($L' = PEt_3$, $L = PPh_3$, ~ 50% dispropor-



SCHEME 2.
(a) ^{1}H NMR: $\delta(CH_3)$ 0.35, $^2J(PtH)$ 80 Hz, $^3J(PH)$ 4.5 Hz; (in CD_2Cl_2)
^{31}P NMR: $\delta(PEt_3)$ 13.07, $J(PtP)$ 3738 Hz.
(b) ^{1}H NMR: $\delta(C(CH_3))$ 1.86, $\delta(COOCH_3)$ 3.24, 3.47;
^{31}P NMR: $\delta(PEt_3)$ 4.32, $J(PtP)$ 3462 Hz.
(c) ^{1}H NMR: δ 0.67, $J(PH)$ 5.5 Hz.

tionation, *cis*, ^{1}H NMR $\delta(CH_3{}^1)$ 0.12, *J*(PH) 7 Hz, *J*(PtH) 67 Hz; $\delta(CH_3{}^2)$ 0.28, *J*(PH), 7 Hz, *J*(PtH) 67 Hz; ^{31}P NMR $\delta(PEt_3)$ 4.87, *J*(PtP) 1848 Hz; $\delta(PPh_3)$ 24.78, *J*(PtP) 1919 Hz, *J*(PP) 12.2 Hz; for L′ = PEt_3, L = $AsPh_3$ no disproportionation, *cis*, ^{1}H NMR $\delta(CH_3)$ 0.28, *J*(PH) 7 Hz, *J*(PtH) 64 Hz; ^{31}P NMR δ 7.34, *J*(PtP) 1941 Hz; for L′ = PEt_3, L = $SbPh_3$, no disproportionation, *cis*). The dimethyl complexes are stable and do not disproportionate in $CDCl_3$ over a period of 3 days. Some reactions of *cis*-$PtMe_2(PEt_3)(AsPh_3)$ are summarized in Scheme 2.

We have thus demonstrated that the low symmetry of mixed ligand complexes of platinum(II) can be preserved and even enhanced through a wide variety of reactions. The stability of the species such as $PtRCl(PEt_3)(AsPh_3)$ (R = H or CH_3) containing four different ligands on platinum, and the fact that its five coordinate olefin complex, $PtRCl(PEt_3)(AsPh_3)$(olefin), either isolable or occurring only as a reaction intermediate, would totally lack symmetry, offers many interesting possibilities. Further investigations of such complexes, including their possible use as catalysts, are under way.

We thank the Natural Sciences and Engineering Research Council of Canada for continued financial support.

References

1 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1955) 3858; (1957) 2445.
2 F.H. Allen and S.N. Sze, J. Chem. Soc. A, (1971) 2054.
3 C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc. Dalton, (1978) 1288.
4 H.C. Clark and H. Kurosawa, J. Organometal. Chem., 36 (1972) 399.